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A Kinetic Model for Toluene Oxidation Comprising Benzylperoxy Benzoate Ester as Reactive Intermediate in the Formation of Benzaldehyde

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A Kinetic Model for Toluene Oxidation Comprising Benzylperoxy Benzoate Ester as Reactive Intermediate in the Formation of Benzaldehyde

J.A.A. Hoorn, P.L. Alsters, and G.F. Versteeg

Abstract

During the oxidation of toluene under semibatch conditions, the formation of benzyl alcohol is initially equal to the rate of formation of benzaldehyde. As the overall conversion increases the benzyl alcohol concentration at first decreases much faster than benzaldehyde, but this decrease slows down causing the benzyl alcohol concentration to reduce to zero only very slowly. To account for this phenomenon a new reaction pathway has been proposed where the formation of benzaldehyde out of benzylhydroperoxide is catalysed by benzoic acid. Incorporation of this new reaction in a model improves the description of benzyl alcohol concentration profiles while maintaining good predictions for benzaldehyde and benzoic acid.

KEYWORDS: benzoic acid, autoclave, radicals, network, mechanism

1. INTRODUCTION

Toluene oxidation is a reaction system in which chemistry, kinetics, thermodynamics, transport processes and hydrodynamics interact in a complex fashion. Although the initial development of the process took place already more than 50 years ago (Palmer and Bibb, 1942; Hearne et al., 1951) and a lot of details have been published (Keading et al., 1965; Mulkay and Rouchoud, 1967; van Goolen and van den Berg, 1967), there is still room for improvement especially in the area of integration of the aforementioned disciplines. As an integrating tool, modelling is very suitable to perform that task. Early model developments have in common that the main focus is on the kinetics and that other process items are not considered. The interaction of the mass transfer of oxygen with the toluene oxidation reactions has been addressed by Hoorn et al. in a recent paper (Hoorn et al., 2005). In order to develop a model suitable for combination with more detailed mass transfer phenomena the kinetic mechanism is simplified to interactions between the basic components. The simplest model possible is derived from the overall reaction stoichiometry (Figure 1).

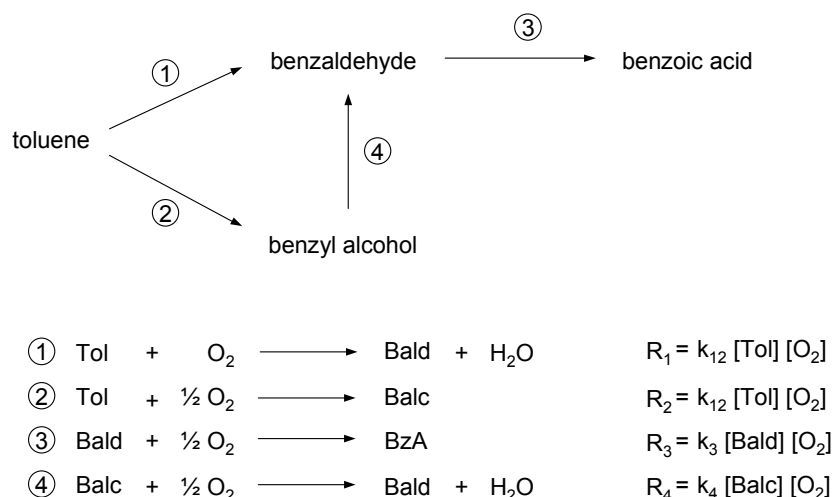


Figure 1. Basic model kinetic scheme

estimated using literature correlations. The values for the specific surface area were estimated with the correlation of Shridhar and Potter (1980), diffusion coefficients were estimated with the correlation of Wilke-Chang (1955). Mass transfer coefficients were calculated for water with the equation of van 't Riet (1979). To translate the mass transfer coefficients from water at ambient conditions to toluene at reactor conditions, it was assumed on basis of the penetration theory from Higbie (1935) that the mass transfer coefficient varies with the square root of the diffusion coefficient as shown in Equation (1).

$$\frac{k_L(\text{toluene}, 150^\circ\text{C})}{k_L(\text{water}, 25^\circ\text{C})} = \sqrt{\frac{D(\text{toluene}, 150^\circ\text{C})}{D(\text{water}, 25^\circ\text{C})}} \quad (1)$$

The reactor models have been programmed in Aspen Custom Modeler. The equations are given in Appendix 1. Within Aspen Custom Modeler a least squares method is applied to minimize the differences between experimental values and model calculations. The parameters for this basic kinetic model have been determined in an experimental set-up comprising a reactor/condenser system operated in a continuous mode (Hoorn et al., 2005). This is suitable for testing under industrial conditions, but not optimal for kinetic parameter estimations. To validate the model under different conditions a number of experiments have been performed in a semibatch laboratory autoclave. In these experiments oxygen was the only reactant that was supplied continuously.

It has to be noted that the expressions for the reaction rates of the above model were generated on basis of a best-fit procedure during parameter estimations. In particular the oxygen dependence in the expressions, i.e. first order is in contrast with the general view on autoxidation reaction rates: zero-th order with respect to oxygen concentration (Helferrich, 2001). However, with the implementation of the mass transfer rate of oxygen substantially improved results were obtained when the oxygen concentration was incorporated in the equations. Other model parameters than those for the kinetic rate constants have been

2. EXPERIMENTAL

A Parr autoclave is used for toluene oxidation experiments. The reactor set-up comprises a batch liquid and a continuous gas phase. The Parr autoclave has a volume 250 ml, is equipped with a mechanical stirrer and has a sample device. The autoclave is equipped with a reflux condenser of sufficient capacity with respect to the heating power of the reactor jacket. The reflux rates are fairly high in a typical experiment. Application of a cold trap after the condenser shows that the amount of condensable components passing through the reflux condenser is very little compared to the total liquid content. A scheme is shown in Figure 2.

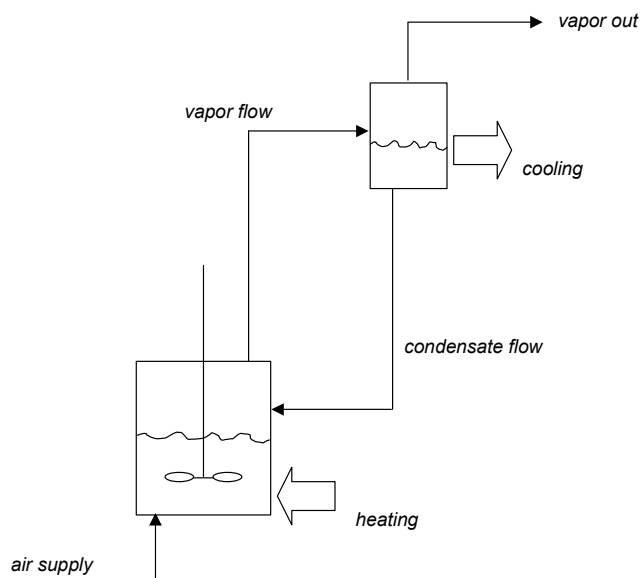


Figure 2. Principles of toluene oxidation in Parr autoclave

combination of methods. The weight for benzyl alcohol was fixed at a value of 1, the benzaldehyde weight was adjusted to 0.8 on basis of the (average) slightly higher mass fractions. The weight for benzoic acid was determined by trial and error; the results of several estimated parameter sets with varying benzoic acid weights showed that best results were obtained with a value of 0.2.

The statistical output of the results is given as sums of the squared residuals of model prediction and experimental values (SSR). Also the sum of squared observations (SSO) are given as reference for the SSR. These definitions and as well as the standard deviation of data are given in Appendix 1. The standard deviations for parameters are the variances as calculated by the standard procedure provided by Aspen Custom modeler (covariance matrix calculation from Jacobian and Hessian matrices of the objective function and the parameters).

The temperature for the experiments was in the range of 155 – 165 °C and the total pressure in the autoclave was kept constant at 7 bar. Air was applied as gas feed. The oxygen concentration in the off-gas flow was kept below 8 vol% for safety reasons. Five experiments were performed at a gas flow of 50 NL/hr. Oxygen concentrations were typically in the range of 2 vol%. The differences in induction period were taken into account by taking the initial increase in temperature in the liquid as the starting time of the reaction.

The estimations of kinetic parameters were performed by a least squares minimization procedure. The objective function was the sum of the weighted differences between model and experimental observed mass fractions in the liquid for the components benzyl alcohol, benzaldehyde and benzoic acid. Toluene was not included in the objective function because the toluene concentrations were not analysed but derived from the mass balance. The weights of the experimental values for the mass fractions were determined by a

3. RESULTS

The results from 5 runs with identical settings are listed in Table 1. The toluene concentration is not analysed but calculated from the balance.

Table 1. Experimental data

Experiment#	Time	BzA (wt%)	Balc (wt%)	Bald (wt%)
1	7	0.10	0.54	0.51
	15	0.91	1.41	1.28
	27	3.51	1.70	2.07
	41	7.28	1.26	2.59
	60	13.04	0.78	2.49
	79	21.36	0.78	2.20
	95	25.72	0.83	2.10
	104	27.87	0.82	2.04
2	9	0.13	0.58	0.60
	20	1.63	1.33	1.70
	34	5.08	1.04	2.41
	49	9.05	0.85	2.40
	64	13.49	0.69	2.41
	79	18.33	0.59	2.33
	98	23.51	0.57	2.17
	106	25.93	0.58	2.13
3	1.25	0.04	0.19	0.14
	6.5	0.22	0.84	0.70
	9.8	0.64	1.29	1.25
	18	2.12	1.46	1.86
	44	9.05	0.74	2.60
	60.5	14.01	0.51	2.49
	89	18.64	0.41	2.34
	119	29.77	0.34	2.03
4	0.5	0.00	0.02	0.03
	5.8	0.04	0.46	0.53
	10	0.33	0.96	1.07
	20	1.95	1.34	1.98
	30.25	4.43	0.98	2.48
	45	8.57	1.19	2.29
	59.8	12.09	0.61	2.46
5	6.35	0.14	0.64	0.49
	12.2	0.66	1.27	1.19
	26	3.76	1.39	2.36
	45.8	9.21	0.59	2.68
	63	14.57	0.47	2.41

With the basic model the simulation results for benzaldehyde and benzoic acid are in good agreement with experiments. The description for benzyl alcohol was not satisfying, it proved not to be possible to qualitatively describe the "camel hump" in the concentration of benzyl alcohol as is shown in Figure 3.

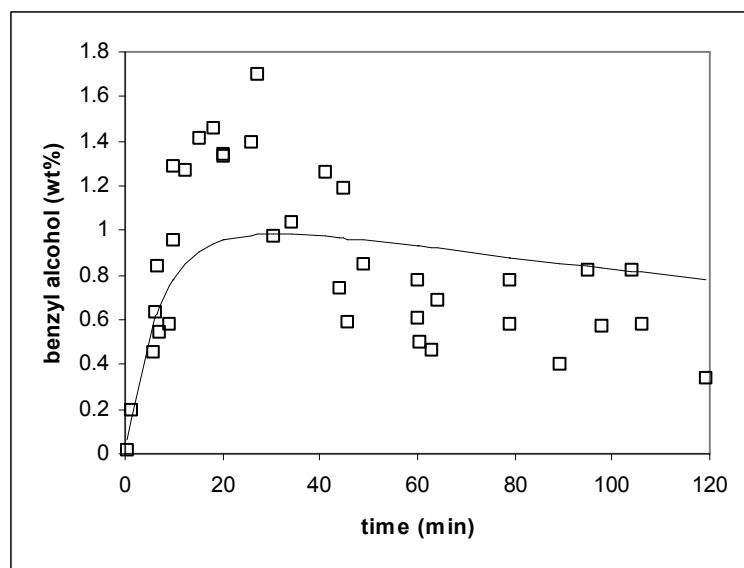


Figure 3. Model prediction versus experimental values for benzyl alcohol, basic model

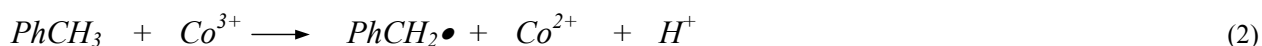
The results presented in Figure 3 clearly suggested that some adaptation on the basic model was required to improve the model prediction for benzylalcohol. One of the possible routes was to change the reaction order coefficients and modify the reaction rate expressions, for example to a more flexible power law. This option was not preferred because the relation of power law expressions to chemical or mass transfer effects is difficult to make. In other words, power law models are not convenient when kinetic expressions are to be derived from chemical principles. Instead, it was preferred to extend the basic model with an effect that occurs preferentially at higher conversions. To identify possible reaction pathways where such effects can occur (part of) the toluene oxidation reaction network is explained in the next section.

4. TOLUENE OXIDATION REACTION NETWORK

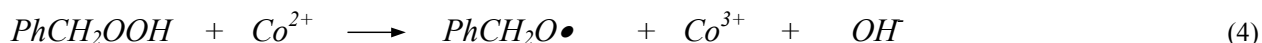
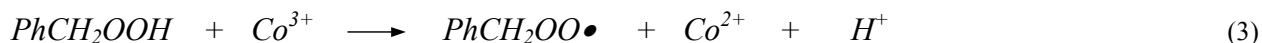
Bukharkina and Digurov (2004) published a comprehensive review on the field of the kinetics and chemistry on liquid-phase oxidations. This field can be subdivided into three main systems: metal catalysed oxidation in non-polar solvents, oxidation in acetic acid as solvent and oxidation in presence of bromide catalysts. Each of the reaction systems has a number of particular properties, but all systems have in common that the reactions proceed through radical intermediates. These radical reactions are part of a network comprising initiation, propagation and termination steps. In addition, non-radical reaction steps also can occur.

4.1. Initiation

Chain-initiating benzyl radicals are generated from toluene by cobalt(III) through one-electron oxidation (Morimoto and Ogata, 1967) as shown in Equation (2).



Peroxides in general are considered as radical initiation sources. The decomposition of peroxides is catalysed by cobalt(II)/cobalt(III) in a Haber-Weiss redox cycle (Helfferich, 2001), Equation (3) and (4).



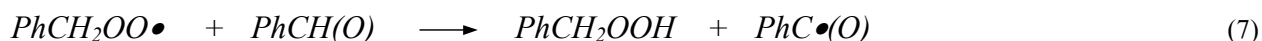
The role of cobalt in the autoxidation of toluene and related components is not limited to these reactions (Scott and Chester, 1972; Kagami, 1968). More examples of cobalt interactions are given in the next paragraphs

4.2. Propagation

Independent of the specific reaction system, all mechanisms presented in literature comprise a diffusion controlled oxygen-coupling reaction with benzyl radical to form a peroxy radical (Bhattacharya et al., 1973; Quiroga et al., 1980; Gabelle and Clément, 1968; Korthals Altes and van den Berg, 1966; Ivanov et al., 1983) as shown in Equation (5).



This peroxy radical can abstract hydrogen from any suitable substrate but most often it will be from toluene or benzaldehyde (Equation (6) and (7)). Similar reactions also occur with the benzoyl radical instead of the benzyl radical as shown in Equations (8) to (10).



The formed perbenzoic acid takes part in the oxidation of benzaldehyde to benzoic acid (Baeyer-Villiger reaction, see next paragraph). Perbenzoic acid can also be decomposed to benzoic acid by Co(II) through an overall reaction described by Hendriks et al. (1978a), see Equation (11).



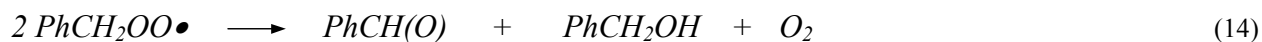
Some other radicals are also involved in transfer reactions producing a stable product, for example the reaction of benzyloxy radical (formed in the initiation reactions) abstracts hydrogen from toluene or benzaldehyde to form benzyl alcohol, Equation (12) and (13).



4.3. Termination and Sequential Reactions

Experiments on toluene oxidation are mostly carried out with high oxygen concentrations in the gas phase. The reaction rate of C-centered radicals with oxygen is in general very fast. Traces of oxygen in the liquid decrease the concentration of C-centered radicals drastically. For these reasons termination products from C-centered radicals such as benzyl radicals only occur at very low oxygen pressures.

The primary termination reaction proceeds according to a Russell mechanism (1957) between two benzylperoxy radicals forming oxygen, benzyl alcohol and benzaldehyde (Equation(14) and Figure 4).



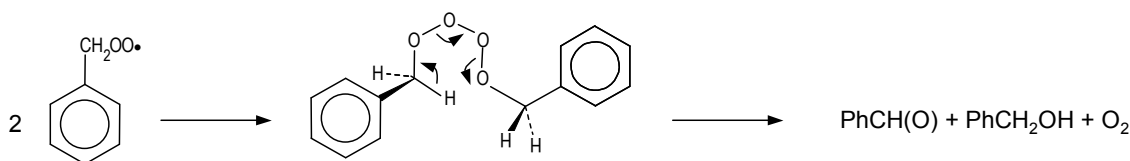


Figure 4. Russell mechanism for benzylperoxy radical termination reaction

The oxidation of benzaldehyde to benzoic acid is a Baeyer-Villiger type reaction. In Figure 5 it is shown that perbenzoic acid oxidizes benzaldehyde forming two benzoic acid equivalents (Hendriks et al., 1978b).

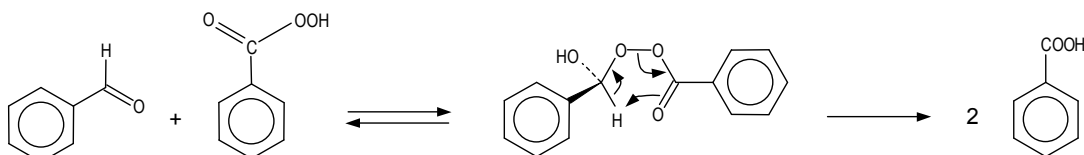
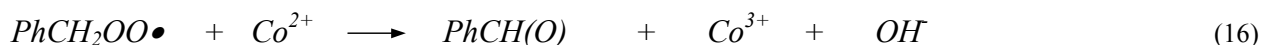
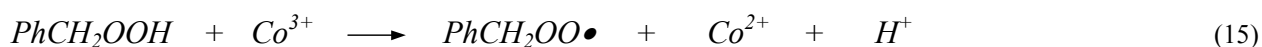


Figure 5. Baeyer-Villiger reaction

Formation of benzaldehyde from benzylhydroperoxide proceeds through a Co(II)/Co(III) cycle as shown in Equations (15) and (16).



A pathway involving a hydrogen abstraction from the benzylic position of benzyl alcohol under the influence of Co(III) also accounts for benzaldehyde formation. The radical intermediate ("center-OH radical") reacts with oxygen to form an peroxy hydrate which decomposes in turn to hydrogen peroxide and benzaldehyde (Figure 6).

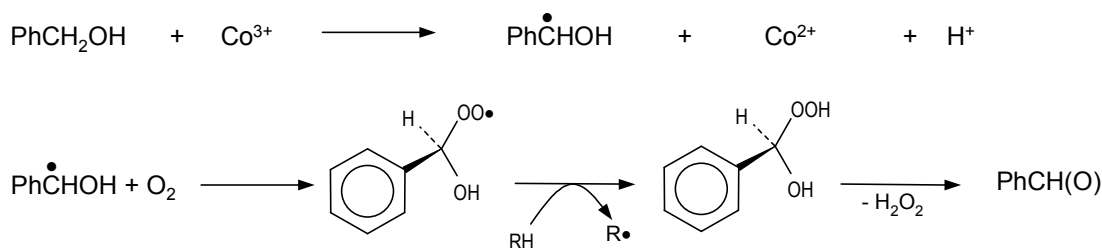


Figure 6. Oxidation of benzyl alcohol to benzaldehyde

To summarize the (main) reactions pathways, a simplified scheme is presented in Figure 7. All secondary transformations that occur in multiple reactions such as the cobalt oxidations or reductions and the hydrogen abstraction reactions have not been taken into account in the scheme for clarity purposes.

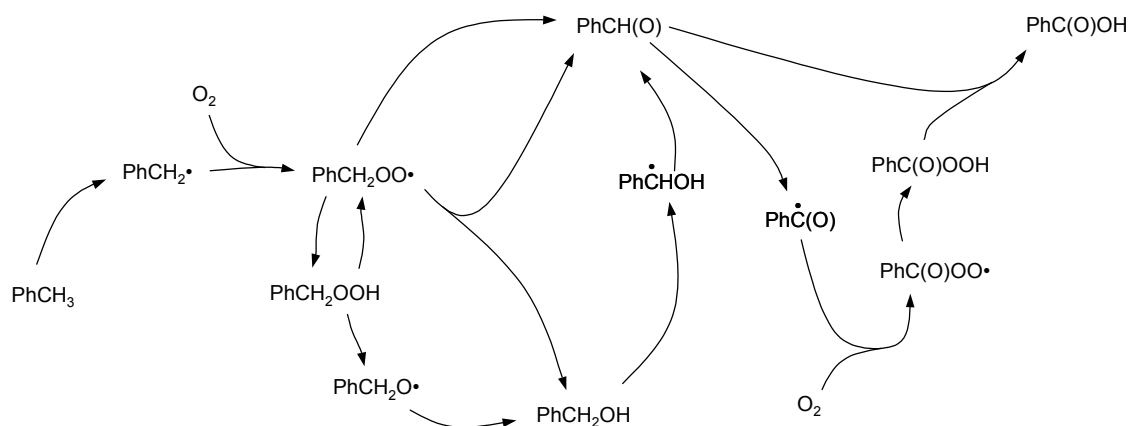


Figure 7. Reaction network for toluene oxidation showing main reactions

Only a fraction of the reaction rates of the reactions mentioned in Figure 7 are known. In a series of papers by Howard and Ingold reaction rates for a variety of alkyl aromatic compounds have been determined (1967). The developments on the estimation of reaction rate constants through molecular modelling are very promising but still not that accurate for predicting the pre-exponential factors (van Speybroeck and Meier, 2003). The number of reactions studied in detail is also quite limited still. The reactions shown in Figure 7 have no indication for a decreased formation or increased reaction of benzyl alcohol at higher conversions. The primary component formed at high conversion is benzoic acid. It is postulated here that benzoic acid reacts with benzylhydroperoxide to form an intermediate peroxyester (Figure 8).

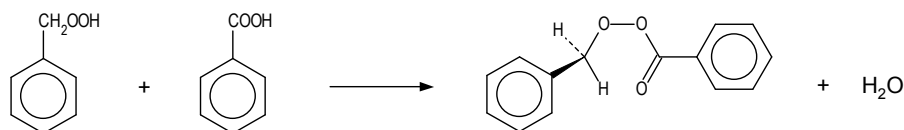


Figure 8. Formation of benzylperoxy benzoate ester

The peresterification is followed by a decomposition to form benzaldehyde and benzoic acid. The postulated six-membered transition state of the perester decomposition strongly resembles the commonly accepted transition state for the Baeyer-Villiger type of rearrangement shown in Figure 9:

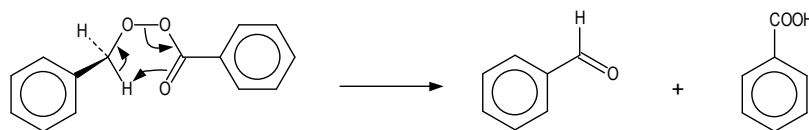


Figure 9. Formation of benzaldehyde by benzylperoxy benzoate ester decomposition

In this way the formation of benzaldehyde will have a dependency on the benzoic acid concentration, i.e. as the reaction progresses the rate of benzaldehyde formation will be increased relative to that of benzyl alcohol. Note that benzoic acid effectively acts as a catalyst for benzylhydroperoxide dehydration to benzaldehyde, since it is regenerated in the peroxyester decomposition step.

5. EXTENDED MODEL

To incorporate the concept of a peroxyester intermediate benzylhydroperoxide (peroxide) and its radical equivalent are added to the basic kinetic scheme (Figure 10).

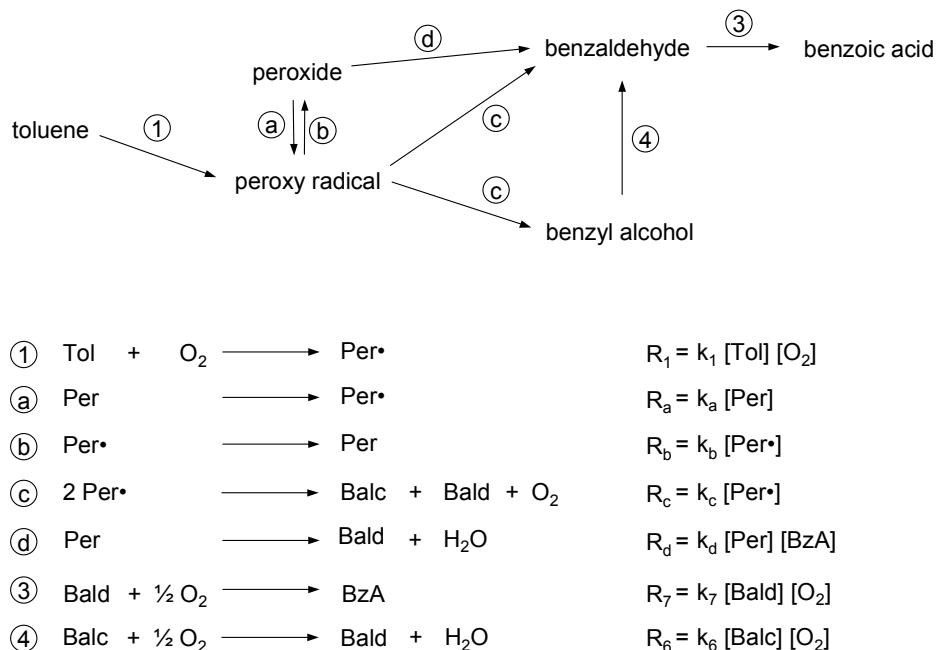


Figure 10. Extended model kinetic scheme

The naming of the rate constants in comparison to the basic scheme in Figure 1 has been kept identical as much as possible. The rate constants that are involved in equations comprising reactive intermediates have been designated letters instead of numbers because these constants will be simplified later.

To eliminate the reactive intermediates from the rate expressions, no distinction is made between initiation and termination rates on one hand and propagation rates on the other hand (which is commonly applied in reducing radical networks (Helfferich, 2001) because several components are involved in both radical and non-radical reactions. Instead, the peroxy radical and peroxide concentrations are eliminated with an overall steady-state assumption, see Equation (17) and (18).

$$\text{peroxy radical:} \quad R_1 + R_a = R_b + 2 \cdot R_c \quad (17)$$

$$\text{peroxide:} \quad R_b = R_a + R_d \quad (18)$$

In order to reduce the number of parameters, it is also assumed that the radical reactions (a) and (b) are much faster than the other reactions. The peroxy radical and the hydroperoxide maintain in equilibrium throughout the reaction progress. On basis of Equations (17) and (18), it is not difficult to derive equations for R_c and R_d in which the intermediates have been eliminated (see Appendix 2). The explicit expressions for R_c and R_d allow all component reaction rates to be expressed as functions of observable concentrations:

$$R_c = \frac{k_1 \cdot [\text{Tol}] \cdot [\text{O}_2]}{2 + k_2 \cdot [\text{BzA}]} \quad (19)$$

$$R_d = \frac{k_1 \cdot k_2 \cdot [\text{BzA}] \cdot [\text{Tol}] \cdot [\text{O}_2]}{2 + k_2 \cdot [\text{BzA}]} \quad (20)$$

6. COMPARISON OF THE MODELS

The modified reaction rate expressions after optimising the kinetic parameters improves the benzyl alcohol description indeed substantially as is shown in Figure 11 (Right side). The comparison of the results generated by the two models is shown in graphical form in Figures 11-14. The values for the kinetic parameters of the two models are given in Table 2 and 3. The interval values in Table 3 are the standard deviations. The correlation matrices show how much the parameters dependent on each other. The statistics on the data points and the goodness-of-fit are given in Table 4.

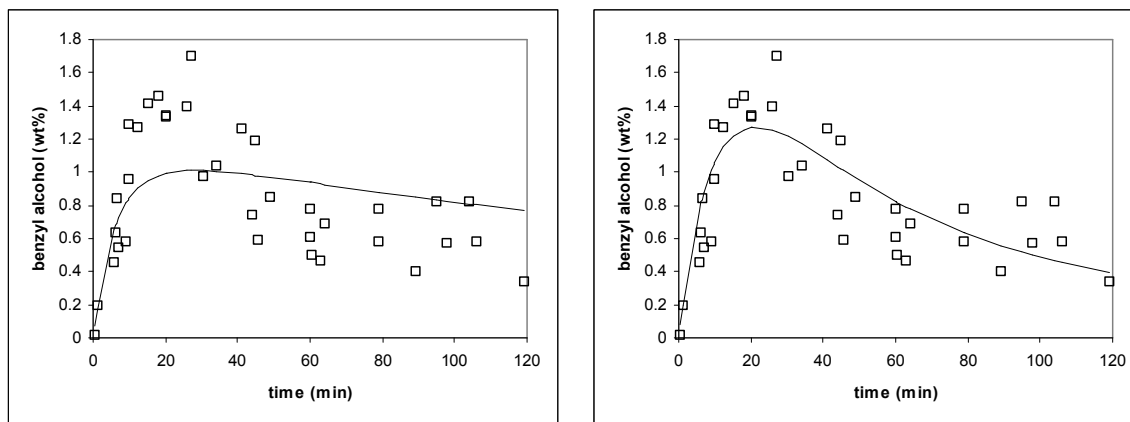


Figure 11. Model prediction (line) versus experimental values (symbol) for benzyl alcohol concentration as function of reaction time. Left: basic model. Right: extended model

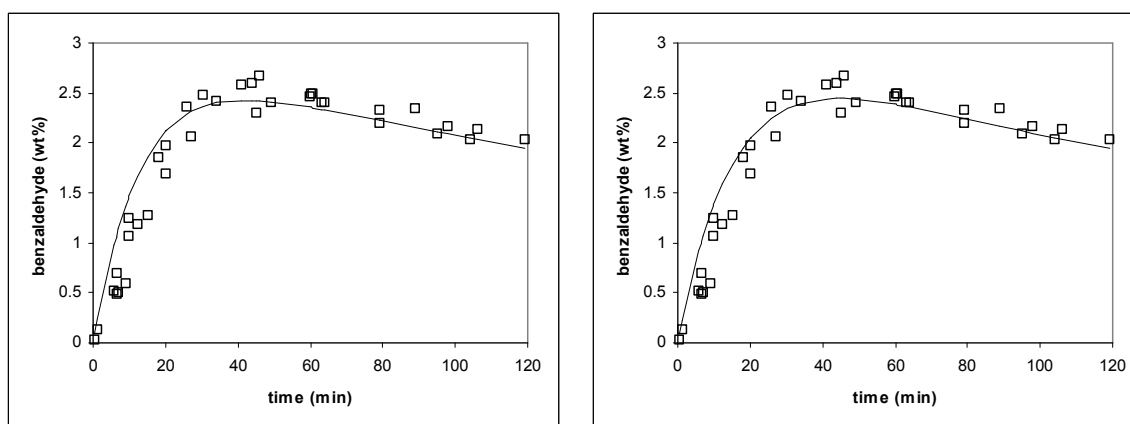


Figure 12. Model prediction (line) versus experimental values (symbol) for benzaldehyde concentration as function of reaction time. Left: basic model. Right: extended model

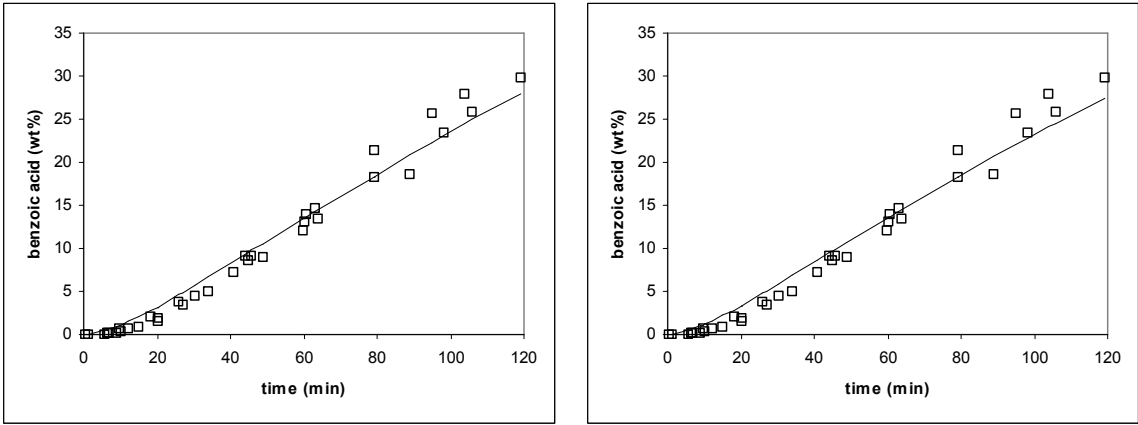


Figure 13. Model prediction (line) versus experimental values (symbol) for benzoic acid concentration as function of reaction time. Left: basic model. Right: extended model

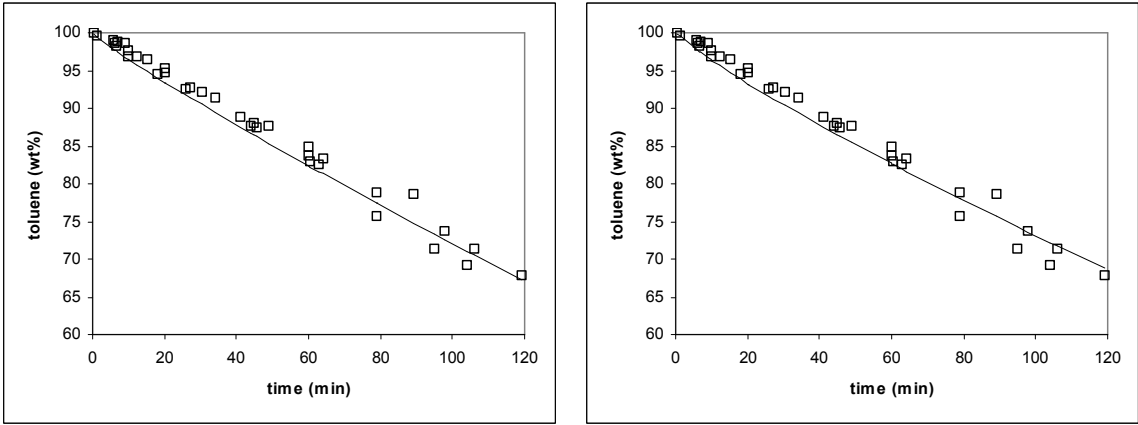


Figure 14. Model prediction (line) versus experimental values (symbol) for toluene concentration as function of reaction time. Left: basic model. Right: extended model

Table 2. Kinetic parameters basic model

Parameter values			Correlation matrix			
				k_{12}	k_3	k_4
k_{12}	0.018 ± 0.002	l/mol/s	k_{12}	1		
k_3	1.52 ± 0.15	l/mol/s	k_3	0.99	1	
k_4	1.93 ± 0.20	l/mol/s	k_4	0.96	0.95	1

Table 3. Kinetic parameters extended model

Parameter values			Correlation matrix				
				k_1	k_2	k_3	k_4
k_1	0.020 ± 0.002	l/mol/s	k_1	1			
k_2	0.051 ± 0.022	l/mol	k_2	-0.12	1		
k_3	0.87 ± 0.06	l/mol/s	k_3	0.97	-0.07	1	
k_4	0.65 ± 0.08	l/mol/s	k_4	0.46	-0.92	0.40	1

Table 4. Statistical output for both models

Component	Weight	Statistic ¹⁾	Experimental data	Basic model	Extended model
Benzyl alcohol	1	SSO	30.6		
		SSR		3.33	1.79
		SDD		0.31	0.23
Benzaldehyde	0.8	SSO	139		
		SSR		3.01	2.28
		SDD		0.24	0.21
Benzoic acid	0.2	SSO	6056		
		SSR		66	79
		SDD		0.28	0.31
Toluene	0	SSO	270213		
		SSR		536	661
		SDD		-	-

1) SSO = Sum of Squared Observations, SSR = Sum of Squared Residuals, SDD = Standard Deviation of Data

7. DISCUSSION

The estimation of kinetic parameters on the batch autoclave experiments has been successful for both model versions, but the extended model with benzoic acid concentrations in the reaction rate expressions gives a better qualitative and quantitative description of the benzyl alcohol concentrations. Also with regard to the description of benzaldehyde the extended model has a slightly better performance than the basic model as can be seen from the statistical values in Table 4. The differences are not very substantial however; comparing the ratio of the sum of squared residuals and the sum of squared observations the improvement for benzaldehyde is a decrease from 1.3% to 0.9% in favour of the extended model. The benzoic acid concentration is better described by the basic model. The changes are not very substantial as can be verified by the visual comparison of Figure 13 and Figure 14. For both models it is observed that the concentrations for benzaldehyde appear to be somewhat lower than the experimental values. By changing the weights for the different datasets in the parameter estimation procedure it is possible to improve the description for benzaldehyde by a few percent but at the same time the good fit for benzyl alcohol is lost. Extension of the number of experiments and increasing the variation in the reaction conditions should be the strategy to improve the model in this respect.

The extended model includes a peresterification of benzylhydroperoxide and benzoic acid as an important step in order to describe the kinetic behaviour of benzyl alcohol properly. This assumption is reasonable, since peroxyesters can be prepared through condensation of a hydroperoxide with carboxylic acid (Sanchez and Meyers). Other models, such as those described by Bukharkina and Digurov (2004), appear to be able to describe the kinetics of benzyl alcohol properly. Unfortunately, the lack of details with respect to their model and experimental conditions precludes a more accurate comparison with our extended model.

Five experiments with identical conditions provide a useful estimation of the accuracy of the results. As can be seen from Figure 12 and Figure 13 the spread in the benzyl alcohol values is larger than the benzaldehyde percentages. This is caused by a combination of factors. The concentrations for benzyl alcohol are a factor 2 lower than benzaldehyde after the initial reaction period. Benzyl alcohol is also more difficult to analyse accurately than benzaldehyde. A third reason is the involvement of benzyl alcohol in side reactions such as esterification with benzoic acid to benzyl benzoate.

Although the limited number of and variation in experiments make it impossible to estimate a larger number of kinetic parameters, it is questionable whether all kinetic parameters of a reaction network presented in Figure 7 can be determined on the basis of experiments alone. The most promising route to manipulate complex reaction networks appears to be a synthesis of experiments and molecular modelling. One of the major challenges is to maintain the balance between the number of parameters and the predictive quality of the model. At the same time it is very much desired to increase the number of significantly determined parameters at the lowest experimental effort.

On the basis of the theoretical correlations it was found that the high rotational speed of the autoclave stirrer and the small liquid volume gave high values for the mass transfer coefficient, making the exact value for mass transfer coefficient not very critical. In a previous investigation (Hoorn et al., 2005) it was found that the oxidation of toluene is a slow reaction with respect to mass transfer. In combination with a sufficiently high oxygen concentration in the gas phase it can therefore be concluded that the mass transfer for oxygen is not important in these experimental settings. However, the models are set-up in such a way that also non-ideal conditions can be described.

8. CONCLUSIONS

In a batch operated autoclave the benzyl alcohol concentrations are initially increasing equally fast as benzaldehyde. As the oxidation of toluene progresses, the benzyl alcohol concentration diminishes faster in comparison with benzaldehyde, but the benzyl alcohol concentration approaches zero only very slowly at longer reaction times. In order to describe this behaviour by means of a model a dependency on the benzoic acid concentration is suggested. Through the hypothesis that the decomposition of benzylhydroperoxide to benzaldehyde is catalysed by benzoic acid the formation rate of benzaldehyde is increased relative to benzyl alcohol at higher benzoic acid concentrations. Through estimation of the kinetic parameters the modifications in the model indeed improve the description of the benzyl alcohol concentration profiles observed during the oxidation of toluene.

NOTATION

c	concentration in liquid phase, mol/l
F	flow, mol/s
k	kinetic rate constant, 1/s or l/mole/s
k^p_{flow}	constant for controlling flows, mol/bar/s
k_{flow}	constant for controlling flows, mol/l/s
$k_L a$	volumetric liquid side mass transfer coefficient, s ⁻¹
m	mass in liquid phase, g
M_r	molar mass, g/mol
n	number of moles, mol
n_{obs}	number of observations, -
n_{par}	number of parameters, -
P	pressure, bar
R	reaction rate, mol/l/s
V	volume, l
w	weight factor for estimation, -
x	mole fraction in liquid phase, mol/mol
y	mole fraction in gas phase, mol/mol
Y_{calc}	calculated variable, -
Y_{exp}	observed variable, -

Greek

ρ	density, mol/l
ϕ	fugacity coefficient, -

Subscripts

i	component
gas	vapor phase
vap	vapor phase
liq	liquid phase
tot	total
nv	non-volatiles
set	set point

Superscripts

in	feed stream
out	exit stream
sat	saturated

Abbreviations

Balc	benzyl alcohol
Bald	benzaldehyde
BzA	benzoic acid
Per	benzylhydroperoxide
Per•	benzylperoxy radical
Tol	toluene

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APPENDIX 1. MODEL EQUATIONS AND STATISTICAL DEFINITIONS

Kinetics – basic

$$R_1 = k_{12} \cdot c_{TOL} \cdot c_{O_2}$$

$$R_2 = k_{12} \cdot c_{TOL} \cdot c_{O_2}$$

$$R_3 = k_3 \cdot c_{BALD} \cdot c_{O_2}$$

$$R_4 = k_4 \cdot c_{BALC} \cdot c_{O_2}$$

$$R_{BALC} = R_2 - R_4$$

$$R_{BALD} = R_1 - R_3 + R_4$$

$$R_{BzA} = R_3$$

$$R_{H_2O} = R_1 + R_4$$

$$R_{O_2} = -R_1 - \frac{1}{2} \cdot (R_2 + R_3 + R_4)$$

$$R_{TOL} = -R_1 - R_2$$

Kinetics – extended

$$R_1 = k_1 \cdot c_{Tol} \cdot c_{O_2}$$

$$R_c = \frac{k_1 \cdot c_{Tol} \cdot c_{O_2}}{2 + k_2 \cdot c_{BzA}}$$

$$R_d = \frac{k_1 \cdot k_2 \cdot c_{BzA} \cdot c_{Tol} \cdot c_{O_2}}{2 + k_2 \cdot c_{BzA}}$$

$$R_3 = k_3 \cdot c_{BALD} \cdot c_{O_2}$$

$$R_4 = k_4 \cdot c_{Balc} \cdot c_{O_2}$$

$$R_{Balc} = R_c - R_4$$

$$R_{Bald} = R_c + R_d + R_4 - R_3$$

$$R_{BzA} = R_3$$

$$R_{H_2O} = R_d + R_4$$

$$R_{O_2} = -R_1 + R_c - \frac{1}{2} (R_3 + R_4)$$

$$R_{Tol} = -R_1$$

Definitions

$$m_i = n_{liq,i} \cdot M_{r,i}$$

$$(wt\%)_i = 100 \cdot \frac{m_i}{m_{nv}}$$

$$m_{nv} = \sum_i m_i - m_{O_2} - m_{N_2}$$

Reactor

For all components i :

$$\phi_{gas,i} \cdot y_i = \phi_{liq,i} \cdot x_i^{sat}$$

$$n_{gas,tot} \cdot y_i = n_{gas,i}$$

$$n_{liq,tot} \cdot x_i = n_{liq,i}$$

$$c_i = \rho_{liq} \cdot x_i$$

$$c_i^{sat} = \rho_i^{sat} \cdot x_i^{sat}$$

$$F_{gas,i}^{out} = y_i \cdot F_{gas,tot}^{out}$$

$$\frac{dn_{liq,i}}{dt} = F_{liq,i}^{in} + k_L a \cdot V_{tot} \cdot (c_i^{sat} - c_i) + V_{liq} \cdot R_i$$

$$\frac{dn_{gas,i}}{dt} = F_{gas,i}^{in} - F_{gas,i}^{out} - k_L a \cdot V_{tot} \cdot (c_i^{sat} - c_i)$$

Other equations :

$$F_{gas,tot}^{out} = \sum_i F_{gas,i}^{in} + k_{flow} \cdot (P_{tot} - P_{set}) \quad \text{if } P_{tot} \geq P_{set} \quad \text{else } F_{gas,tot}^{out} = 0$$

$$V_{gas} \cdot \rho_{gas} = n_{gas,tot}$$

$$V_{liq} \cdot \rho_{liq} = n_{liq,tot}$$

$$V_{liq} + V_{gas} = V_{tot}$$

$$n_{gas,tot} = \sum_i n_{gas,i}$$

$$n_{liq,tot} = \sum_i n_{liq,i}$$

Cooler

For all components i :

$$\phi_{gas,i} \cdot y_i = \phi_{liq,i} \cdot x_i^{sat}$$

$$n_{gas,tot} \cdot y_i = n_{gas,i}$$

$$n_{liq,tot} \cdot x_i = n_{liq,i}$$

$$c_i = \rho_{liq} \cdot x_i$$

$$c_i^{sat} = \rho_i^{sat} \cdot x_i^{sat}$$

$$F_{gas,i}^{out} = y_i \cdot F_{gas,tot}^{out}$$

$$F_{liq,i}^{out} = x_i \cdot F_{liq,tot}^{out}$$

$$\frac{dn_{liq,i}}{dt} = k_L a \cdot V_{tot} \cdot (c_i^{sat} - c_i) + V_{liq} \cdot R_i - F_{liq,i}^{out}$$

$$\frac{dn_{gas,i}}{dt} = F_{gas,i}^{in} - F_{gas,i}^{out} - k_L a \cdot V_{tot} \cdot (c_i^{sat} - c_i)$$

Other equations :

$$F_{gas,tot}^{out} = k_{flow}^P \cdot (P_{tot} - P_{set}) \quad \text{if } P_{tot} \geq P_{set} \quad \text{else } F_{gas,tot}^{out} = 0$$

$$F_{liq,tot}^{out} = k_{flow}^V \cdot (V_{liq} - V_{set}) \quad \text{if } V_{liq} \geq V_{set} \quad \text{else } F_{liq,tot}^{out} = 0$$

$$V_{gas} \cdot \rho_{gas} = n_{gas,tot}$$

$$V_{liq} \cdot \rho_{liq} = n_{liq,tot}$$

$$V_{liq} + V_{gas} = V_{tot}$$

$$n_{gas,tot} = \sum_i n_{gas,i}$$

$$n_{liq,tot} = \sum_i n_{liq,i}$$

Statistical definitions:

$$\begin{aligned} \text{Sum of Squared Observations,} \quad SSO &= \sum_{i=1}^{n_{obs}} Y_{exp,i}^2 \\ \text{Sum of Squared Residuals,} \quad SSR &= \sum_{i=1}^{n_{obs}} (Y_{exp,i} - Y_{calc,i})^2 \\ \text{Standard Deviation of Data,} \quad SDD &= \sqrt{\frac{\sum_{i=1}^{n_{obs}} (w_i \cdot (Y_{exp,i} - Y_{calc,i}))^2}{n_{obs} - n_{par}}} \end{aligned}$$

APPENDIX 2. SIMPLIFICATION OF REACTION NETWORK

Reaction rate equations:

$$\begin{aligned} R_I &= k_I \cdot [Tol] \cdot [O_2] \\ R_a &= k_a \cdot [Per] \\ R_b &= k_b \cdot [Per\bullet] \\ R_c &= k_c \cdot [Per\bullet] \\ R_d &= k_d \cdot [Per] \cdot [BzA] \end{aligned}$$

Steady state assumption on peroxy radical and peroxide:

$$\begin{aligned} R_I + R_a &= R_b + 2 \cdot R_c \\ R_b &= R_a + R_d \end{aligned}$$

Substitution of the expressions for the reaction rates and some rearrangements gives:

$$\begin{aligned} [Per\bullet] &= \frac{k_I \cdot (k_a + k_d \cdot [BzA]) \cdot [Tol] \cdot [O_2]}{2 \cdot k_a \cdot k_c + (k_b + 2 \cdot k_c) \cdot k_d \cdot [BzA]} \\ [Per] &= \frac{k_I \cdot k_b \cdot [Tol] \cdot [O_2]}{2 \cdot k_a \cdot k_c + (k_b + 2 \cdot k_c) \cdot k_d \cdot [BzA]} \end{aligned}$$

These expressions are substituted in the reaction rates R_c and R_d :

$$\begin{aligned} R_c &= \frac{k_I \cdot k_c \cdot (k_a + k_d \cdot [BzA]) \cdot [Tol] \cdot [O_2]}{2 \cdot k_a \cdot k_c + (k_b + 2 \cdot k_c) \cdot k_d \cdot [BzA]} \\ R_d &= \frac{k_I \cdot k_b \cdot k_d \cdot [BzA] \cdot [Tol] \cdot [O_2]}{2 \cdot k_a \cdot k_c + (k_b + 2 \cdot k_c) \cdot k_d \cdot [BzA]} \end{aligned}$$

When k_a and k_b are much larger than the other constants the equations for R_c and R_d become:

$$R_c = \frac{k_1 \cdot [Tol] \cdot [O_2]}{2 + \frac{k_b \cdot k_d}{k_a \cdot k_c} \cdot [BzA]}$$

$$R_d = \frac{k_1 \cdot \frac{k_b \cdot k_d}{k_a \cdot k_c} \cdot [BzA] \cdot [Tol] \cdot [O_2]}{2 + \frac{k_b \cdot k_d}{k_a \cdot k_c} \cdot [BzA]}$$

The parameters k_a through k_d in these two expressions can be replaced by one independent constant (k_2 for naming convenience) giving the following final expressions for the rate equations:

$$R_c = \frac{k_1 \cdot [Tol] \cdot [O_2]}{2 + k_2 \cdot [BzA]}$$

$$R_d = \frac{k_1 \cdot k_2 \cdot [BzA] \cdot [Tol] \cdot [O_2]}{2 + k_2 \cdot [BzA]}$$